

## RAPID COMMUNICATION

# Porosity superlattices: a new class of Si heterostructures

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**Abstract.** Porosity superlattices have been investigated by transmission electron microscopy, photoluminescence and reflectance spectroscopy. The superlattices were formed on p-type doped Si using two different techniques. Firstly, for homogeneously doped substrates we have periodically varied the formation current density and thereby the porosity. Secondly, the current density was kept constant while etching was performed on periodically doped Si layers. For the first type of superlattices the layer thicknesses were determined by transmission electron microscopy. The results are in good agreement with the values calculated from the etching rate and time. For both types of superlattices, reflectance and photoluminescence spectra show strong modulation due to the periodicity of the superlattice.

Since the middle of the fifties it has been well known how porous Si layers can be formed [1], but interest in porous Si—its microscopic structure and optical properties—has dramatically increased due to reports of photoluminescence (PL) [2] and electroluminescence (EL) [3,4]. Quantum efficiencies of more than 10% for PL and 0.1% for EL stimulated again the idea of Si based optoelectronics and have been the driving force for a lot of research activities over the last two years. Typical luminescence spectra show a broad band with a peak maximum between 550 and 850 nm and a full width at half maximum (FWHM) of more than 100 nm [2]. For the EL it seems nearly impossible to tune the wavelength of the emission peak with the exception of using electrolytical front contacts [5,6]. In this paper we show for the first time that porosity superlattices can act as filters which will reduce the FWHM and shift the maximum of the emitted light in a reproducible way.

Porosity superlattices are a new type of Si based heterostructures which exhibit a periodic variation in depth of the porosity. Despite the continuing debate on the mechanisms of the luminescences—how must the basic quantum size model be modified to explain the luminescences behaviours—porosity superlattices open a wide field of possible applications especially coloured flatscreens made of Si. In addition, porosity superlattices can lead to a better understanding of the reaction kinetics during the formation process of porous Si layers.

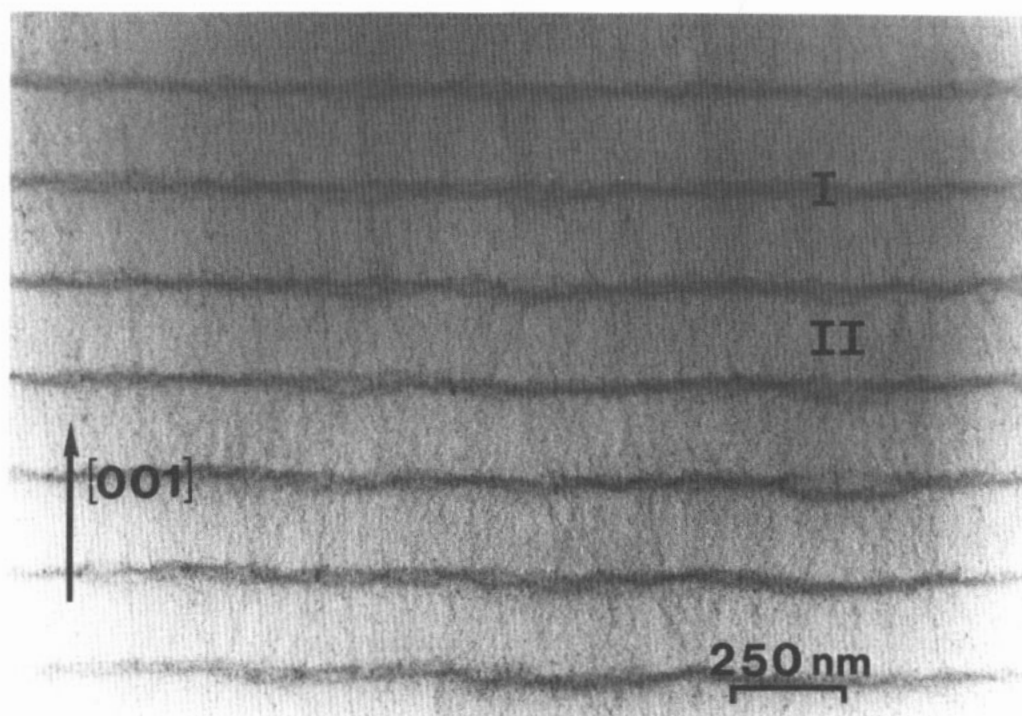
Porosity superlattices can be formed in different ways. First, etch parameters, such as the current density

or the light power, can periodically be changed during the electrochemical etch process. Superlattices formed in this way will be denoted as type I superlattices. Secondly, using periodically doped substrates while keeping the etch parameters constant will also result in the formation of a porosity superlattice (type II). In this communication we report results obtained on both types of porosity superlattices.

For the formation of type I porosity superlattices p-type boron doped Si(100) substrates with resistivities of 0.01 and 0.2  $\Omega\text{cm}$  were used. The anodization was performed in the dark using a mixture of 50% HF with ethanol 1:1. Here, the type I superlattices were formed by varying the current density periodically during the etch process. As current source a Keithley 238 was used which allows a computer controlled etch process.

For the formation of type II porosity superlattices periodically doped films were grown on Si (100) substrates (p-type, 0.01  $\Omega\text{cm}$ ). The doping levels were  $1 \times 10^{17}$  and  $1 \times 10^{19} \text{ cm}^{-3}$ . Two types of periodically doped samples were investigated with single layer thicknesses of 75 and 150 nm. The number of periods was 10 and 5, respectively, resulting in an epitaxial layer thickness of 1.5  $\mu\text{m}$  for both types of sample.

The reflectance of the superlattices was measured under normal incidence using a Perkin-Elmer Lambda 2 spectrometer. For the PL measurements the samples were excited with the 457 nm line of an  $\text{Ar}^+$  ion laser at a power density of 100



**Figure 1.** TEM cross section of a porosity superlattice (type I) formed on p-doped substrate ( $0.2 \Omega \text{ cm}$ ). Layers I: 64% porosity, 20 nm, Layers II: 84% porosity, 200 nm.

$\text{mW cm}^{-2}$ . To avoid photostimulated oxidation [7] PL measurements were performed under ultrahigh vacuum (UHV) conditions. The spectra were taken with a DILOR XY monochromator using a GaAs photomultiplier tube. The PL spectra were corrected for the spectral response of the monochromator. Transmission electron microscopy (TEM) pictures were taken with a Jeol 4000FX using an electron energy of 400 keV.

For a type I superlattice formed by variation of the current density the layer thickness of a single layer is given by the etch rate for a given current density and the particular etch time. For the  $0.01 \Omega \text{ cm}$  substrate material the porosities of a single layer can be varied from about 25 to 75% corresponding to current densities from 10 to  $240 \text{ mA cm}^{-2}$ . However, on  $0.2 \Omega \text{ cm}$  substrates only porous Si layers with porosities between 55 and 75% can be formed, corresponding to current densities between 10 and  $120 \text{ mA cm}^{-2}$ . For both materials the upper porosity limit is given by the mechanical stability of the layers. Porous Si layers with porosities higher than 75% peel off from the substrate due to high strain values. Porosity superlattices are a very promising approach to overcome this problem. Within the superlattice low porosity layers can be used to stabilize high porosity layers which then may have porosities higher than 75%.

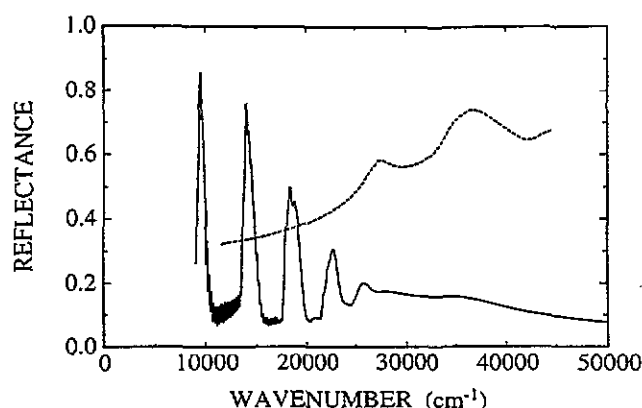
Figure 1 shows a TEM cross section of a type I porosity superlattice with the electron beam parallel to a (110) direction of the sample. In the TEM the lower porosity layers appear dark due to the higher density of the material. The superlattice was formed on p-type doped substrate ( $0.2 \Omega \text{ cm}$ ). Etching was performed by a current sequence of  $19 \text{ mA cm}^{-2}$  for 1 s and  $175 \text{ mA cm}^{-2}$  for 2 s which was repeated 60 times. The

layer thicknesses calculated from these parameters are 16 and 218 nm, respectively. These values are in good agreement with those estimated from TEM which are 20 nm for the low porosity layers and 200 nm for the high porosity layers.

For single layer porous films the above current densities correspond to porosities of 64 and 84%, respectively. Taking the calculated single layer thicknesses into account the mean porosity of the sample has been calculated to 83%. From gravimetric measurements, however, only a mean porosity of 76% is found. This deviation is most likely due to porosity gradients at the interface between layers with different porosities, because for a superlattice with 3 times thicker single layers the measured mean porosity was 79%. The reason for such porosity gradients might be recharging effects of capacities in the etching cell, e.g. due to the Helmholtz layer. The effect of a porosity gradient on the mean porosity of the sample will of course be larger for thinner single layers and can therefore explain the obtained results.

In addition, the porosity of the highly porous single layers of the superlattices has been calculated from the mean porosity obtained by gravimetric measurements, assuming that the porosity of the low porosity layers are known. Values higher than 82% are found, indicating that it is indeed possible to embed otherwise unstable porous layers into mechanically stable porosity superlattices.

The most obvious difference of porosity superlattices as compared to single porous layers is the bright colourful appearance of the superlattice structures. The reason therefore is the very strong modulation of the

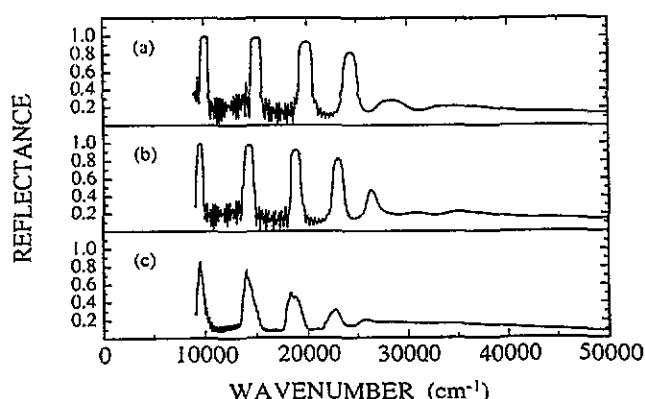


**Figure 2.** Reflectance spectrum of a type I porosity superlattice 20 $\times$  (64% 52 nm, 89% 774 nm) (full line) compared with bulk single crystalline Si (broken line).

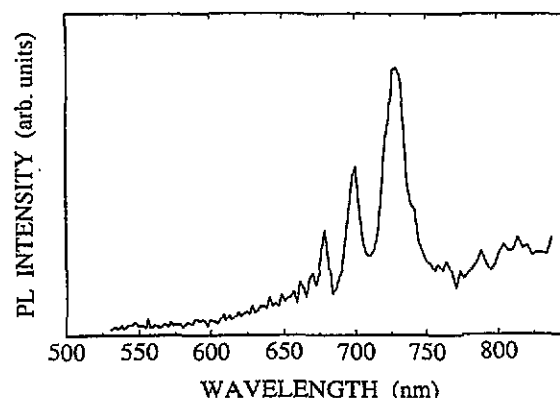
reflectance in the visible spectral range. Figure 2 shows the reflectance spectrum of a type I porosity superlattice measured under normal incidence. The superlattice has been formed on 0.2  $\Omega$  cm p-type doped substrate by repeating a sequence of 19 mA cm $^{-2}$  for 3 s and 207 mA cm $^{-2}$  for 6 s 20 times. According to our results obtained on single porous films these etch parameters correspond to the formation of a superlattice with single layer thicknesses of 48 and 719 nm and porosities of 64 and 89%, respectively. Summing up the layer thicknesses an overall layer thickness of 15.3  $\mu$ m is expected. Cleaving the sample an overall layer thickness of about 16.5  $\mu$ m was found using an optical microscope. This again shows, that in superlattice structures the usual relationship between current density and etch rate is not valid.

In comparison with bulk single crystalline silicon, whose reflectance is shown as a dashed line in figure 2, the reflectance of the superlattice is strongly modulated. For example, the reflectance of a superlattice can be higher by nearly a factor of 3 for energies at around 10000 cm $^{-1}$ . This strong modulation of the reflectance is caused by multiple reflections and interference effects due to the periodicity of the superlattice. The reason for multiple reflections are the different refractive indices of layers with different porosities.

In order to simulate the reflectance spectra the effective dielectric function of the single layers has been calculated within the Bruggeman effective medium theory [8]. This is of course only a first approach because in this simple theory topology effects are not represented adequately, as is the case for the more sophisticated Bergman theory [9]. However, in the Bruggeman theory the only free parameter is the volume fraction of silicon assuming air as the matrix material, which makes it easy to calculate the dielectric function for different porosities. Figure 3 shows a comparison between a measured reflectance spectrum (figure 3(c)) and the corresponding simulations. For the simulation shown in figure 3(a) the porosities are estimated from the etch parameters but the layer thicknesses have been rescaled according to the observed increase of the full layer thickness.



**Figure 3.** Simulation of the reflectance spectrum of a porosity superlattice (type I) using the Bruggeman effective medium theory. (a) 20 $\times$  (64% 52 nm, 89% 774 nm). (b) 20 $\times$  (64% 52 nm, 85% 774 nm). (c) Measurement.

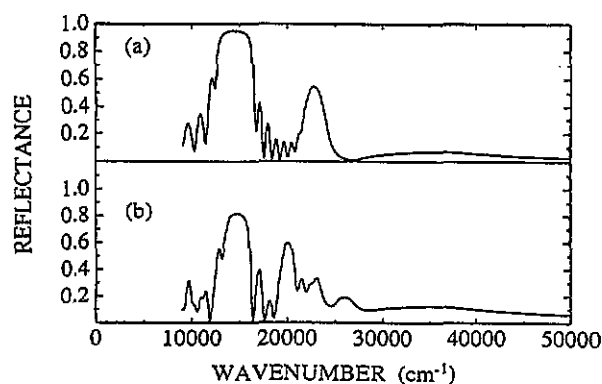


**Figure 4.** Photoluminescence spectrum of a type I porosity superlattice 60 $\times$  (34% 25 nm, 78% 264 nm) formed on p $^{+}$ -doped substrate (0.01  $\Omega$  cm). The main peak has a FWHM of only 17 nm.

Concerning the general lineshape, fairly good agreement between the simulation and the measured spectrum is obtained. However, the peak positions of the maxima in the reflectance do not fit very well. The reason for this might be a deviation of the porosity of the highly porous layers from the value calculated from the etch parameters which might be due to porosity gradients. Decreasing the porosity of the highly porous layers in the simulation from 89 to 85% the agreement can considerably be improved (figure 3(b)). But it must also be kept in mind that the effective dielectric function calculated within the Bruggeman theory using the dielectric function of bulk crystalline Si is only a rough assumption.

Due to the strong modulation of the optical properties also the PL lineshape is changed (figure 4). The porosity superlattice acts as a filter which can be used to narrow the broad luminescence spectrum of porous Si. This is because the emitted light must partially pass through the superlattice and therefore it also undergoes multiple reflections and interferences. The FWHM of the PL peak shown in figure 4 is only 17 nm compared to typical values of more than 100 nm for single porous layers [2].

The modulation of the optical properties can be tuned in a well controlled way. Here, the reflectance spectra



**Figure 5.** Reflectance spectra of type II porosity superlattices. The single layers have a thickness of 75 nm (a) and 150 nm (b). (Formation current density:  $47 \text{ mA cm}^{-2}$ ).

of type II porosity superlattices formed with the same formation current density are shown (figure 5). These reflectance spectra must be compared to the reflectance spectra of the non-porous epitaxial layers which are identical to the one of bulk single crystalline Si shown in figure 2 (dashed line).

In figure 5 structures with short modulation period are due to interferences caused by the total layer thickness of about  $1.5 \mu\text{m}$ . The dominating structures are again due to multiple interferences at the different single layer interfaces. The different values of the reflectance at around  $14000 \text{ cm}^{-1}$  are due to the different number of the single layers. For the sample with 10 periods again a reflectance higher than 95% is obtained.

Because the thicknesses of the single layers differ by a factor of 2 structures occurring at the same energetic position are caused by different orders of interferences. Therefore, the structure at about  $14000 \text{ cm}^{-1}$  is a first order interference in figure 5(a) but a second order interference in figure 5(b). The same explanation holds also for the second and fourth order occurring at about  $23000 \text{ cm}^{-1}$ .

In conclusion for the first time porosity superlattices have been studied. In this paper results obtained on homogeneously as well as on periodically p-type doped substrates are shown. The layer thicknesses of type I superlattices are in good agreement with the calculated values. For thin and extremely high porous layers a deviation of the porosity from the expected values is observed. The reason for this is probably a porosity gradient at the interface between two layers. The reflectance spectra of superlattices show very sharp structures. The origin of these structures are multiple reflections and interferences due to the superlattice structure. Simulations of the reflectance spectra show a rather good agreement with the experiment and can be used to design further superlattice structures for applications. In addition, we have demonstrated the strong influence of the superlattice on the PL lineshape. This offers the possibility to narrow and shift the luminescence of light emitting devices made of porous silicon, e.g., for use in flat coloured displays.

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